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Six-membered ring aliphatic compounds: A search for regularities in phase transitions

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ABSTRACT

Absolute vapor pressures of 1-Cl-adamantane, 2-Cl-adamantane, 1-Br-adamantane, 2-Br-adamantane, as well as of Br-cyclohexane were measured by using the transpiration method. Standard molar enthalpies of sublimation of halogen substituted adamantanes at 298.15 K were derived from vapor pressure temperature dependences. Standard molar enthalpies of solution of adamantane and halogen adamantanes in cyclohexane were measured with a high-precision solution calorimeter. A theoretical procedure based on the solution calorimetry was applied to derive sublimation enthalpies of halogen adamantanes independently. Molar enthalpies of fusion were measured with help of DSC. The consistent data set of phase transitions for each compound was evaluated and used for discussion of structure-property relations in adamantane and cyclohexane derivatives. A simple way to predict enthalpies of vaporization of compounds containing six-membered rings was suggested for practical thermochemical calculations.

1. Introduction

Substituted adamantanes have been used in practice as a basis for structure-based drug design approaches. For example, different adamantane-based inhibitors were developed as effective drugs against influenza [1]. From a theoretical point of view adamantane derivatives are interesting because they are able to form plastic crystals [2,3]. Compounds composed of approximately spherical molecules like adamantanes easily undergo solid–solid phase transitions. Crystals of a highly disordered phase stable just below the melting point (phase I) are generally referred to as plastic crystals [4]. Study of phase transitions in adamantane [5] and its derivatives [6] has been a long-standing goal in our group. In this paper, we focus our interest on studies of the solid-liquid, solid-gas, and liquid-gas phase transitions of halogen-substituted adamantanes. Solid-state phase transitions of halogen-substituted adamantanes below the reference temperature 298.15 K has been a popular endeavor in the recent literature. Calorimetric studies of 1-Cl-adamantane [7,8], 2-Cl-adamantane [9,10], 1-Br-adamantane [7,11–13], and 2-Br-adamantane [10] are already published in the literature and the available enthalpies of phase transitions are mostly in agreement within 1 kJ mol^{-1}. In contrast, the solid-gas phase transitions of halogen-substituted adamantanes are reported only in three papers [11,14,15] and reported sublimation enthalpies seem to be in disarray. Surprisingly, the energetics of the liquid-gas transitions for substituted adamantanes is completely absent. In order to arrange the energetics of phase transition in the halogen adamantanes, we measured temperature dependences of vapor pressures for 1-Cl-adamantane, 2-Cl-adamantane, 1-Br-adamantane, and 1-Br-adamantane with the transpiration method and derived their molar standard enthalpies of sublimation, $\Delta^{g}_{cr}H^{\circ}_{m}$. In order to support transpiration results on sublimation enthalpies we used the independent complementary method based on solution calorimetry measurements [16–19]. Enthalpies of solution at T = 298.15 K of adamantane, 1-Cl-adamantane, 2-Cl-adamantane, 1-Br-adamantane, and 2-Br-adamantane were measured with high-precision solution calorimetry and values of $\Delta^{g}_{cr}H^{\circ}_{m}$ were derived directly at the reference temperature. We used DSC in order to study the thermal behaviour of halogen adamantanes starting from room temperature and including possible

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